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THE EXTRACTION OF TAR ACIDS FROM HIGH TEMPERATURE TAR

DISSERTATION

Submitted in Partial Fulfillment of the Requirements
for the Degree of Doctor of Philosophy
in the Faculty of Pure Science,
Columbia University

BY

THEODORE C. LLOYD, M.S., D.I.C.

L. C.

NEW YORK CITY
1930

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THE EXTRACTION OF TAR ACIDS FROM HIGH TEMPERATURE TAR

ABSTRACT.

The present paper describes the development of a process for the separation of tar acids from coal tar distillates, produced by the destructive distillation of coal at high temperature, which does not involve the use of caustic soda.

The caustic solution is replaced by an aqueous solution of an aromatic organic salt, which is very soluble in water.

With a few notable exceptions, the property of greatly increasing the solubility of tar acids in water, appears to be restricted to the aromatic salts.

Some fourteen of such aromatic salts, all of which are obtainable in quantity and at a sufficiently attractive price, were investigated.

The use of some of these on an industrial scale has been shown to be feasible.

The solubilities of these salts in water at 25° C. has been determined.

The system water-tar acid-sodium toluenesulfonate has been considered in detail.

Steam distillation, which is one of the integral steps of the process, was made the subject of an extended study. By accurate control, this common operation of organic chemistry was made to yield results, which throw new light on the function of organic salt solutions when they act as solvents for tar acids.

THE PROBLEM.

In the distillation of coal tar, the first crude distillate containing tar acids is known as light creosote, middle oil, naphthalene oil, or carbolic oil, the last name being the one in most common use. This fraction is collected roughly in the range 170-230° C. It will in general contain 10% of tar acids and the fraction will represent about 10% of the original tar, the distillate being "cut

over" to creosote oils when the specific gravity reaches a predetermined figure.

The phenol and cresylic acid of commerce are obtained from this carbolic oil by extraction with caustic soda solution. The tar acids are then liberated from the alkaline solution by acidifying with sulfuric acid, or by carbonation with gases of high carbon dioxide content in reaction towers, followed by treatment of the sodium carbonate with lime to recover caustic soda.

This process is the only commercially successful one at the present time.

The present paper relates to the development of a process for extracting tar acids from carbolic oil which eliminates the use of caustic soda, and subsequent treatment with sulfuric acid or carbonation and use of lime. This is effected by using saturated solutions of certain organic salts as extraction media, expelling the extracted tar acids by steam distillation, and concentrating the distillate by fractionation, until a commercially acceptable product is obtained.

COMPETITIVE PROCESSES.

The rapid development of the Bergius hydrogenation process in all its ramifications may be regarded as the most serious threat to the production of tar acids from coal tar.

In view of this, the synthetic method of preparing phenol and cresols by sulfonation of benzene and toluene may be expected to diminish in importance, though always ready to be called into action, when unusual circumstances such as outbreak of war may merit it.

In the carbonization of coal about 50% of the total tar acids, resulting from the primary decomposition of the coal substance, are found in the ammonia liquor, and a like amount in the tar. The recovery of that portion, which occurs in the liquor, has not hitherto proved economical, but has been made compulsory by state officials in some localities, to prevent pollution of inland waters. Such recovery usually comprises preliminary extraction with benzene, followed by recovery of the tar acids by caustic soda solution in a manner similar to that outlined for coal tar

distillates. This phase is receiving much attention at the present time and improvements in procedure may be expected.

Thus, any study which is made of methods which tend to cheapen the production of tar acids from coal tar, will not only be welcome, but may well serve to give new life to an industry doomed to obsolescence, due to competition of the Bergius process.

It was with this in mind that the present research was undertaken.

PREVIOUS WORK.

Attempts to remove tar acids from coal tar distillates by methods which are not based on the use of caustic soda will now pass under review. None of these processes has met with any degree of commercial success.

Pyridine Process.

German patent 406,150 (1926) describes a method of recovering acid oils from tar and tar oils, by treating them with an aqueous solution of a pyridine salt, preferably pyridine sulfate, which is said to form a compound with the cresols. The solution is then steam distilled. Tar acids are recovered from the distillate, which however also contains some pyridine, which must be removed by extracting with acid and liberating with caustic soda. Hence the process does not entirely avoid the use of these materials. The high price of pyridine and its unpleasant odor would also militate against the success of the process.

United States Patent 1,445,668 outlines a similar process.

Sodium Sulfide Process.

Baumann was the first to note the solubility of phenols in sodium carbonate.[2] Fischer remarks[3] that the reaction is too slow to be technically applicable. He has however[3] investigated a method of extracting tar acids from oils with sodium sulfide with the following results.

The acid constituents of coal tar oils are soluble to a certain extent in sodium sulfide. Fischer finds however, that the strongly retarding influence of an active reducing component, present only

in small quantity in coal tar, impedes the extraction. He states that the retarding agent is probably a five or six valent phenol. The tar acids are therefore more soluble in sodium hydrogen sulfide, especially in boiling solution, with evolution of hydrogen sulfide. From the sodium hydrogen sulfide, they may be liberated after cooling, by passage of hydrogen sulfide through it. The extraction thus takes the form of a two stage process. The oils are extracted with hot sodium hydrogen sulfide and the H_2S evolved is passed into the previous extract, which has been cooled. The tar acids are thus liberated from this previous extract with formation of sodium hydrogen sulfide. The solution extracts only the more acidic phenols from crude tar, and from this extract fractional extraction of the phenols becomes possible. The acids may be removed from sodium sulfide solution by extraction with solvents such as ether and benzol.

Superheated Water Process.

Fischer and co-workers have investigated [4, 5] the extraction of tar acids from oils by heating the oils with water in an autoclave to 200-300° C. The vapor pressure of water at 200° is about 25 atmospheres, and at 300° about 85 atmospheres. If a tar oil is heated in an autoclave with an equal quantity of water, with or without stirring, the cresols and xylenols are largely dissolved in the superheated water, the oil, having given up a portion of its phenols to the water, forms a layer above the aqueous solution. This shows that the cresols and xylenols, which are only moderately soluble in water below 100°, are soluble to a considerable extent in water super-heated to 200°. (Sidgwick, Spurrell and Davies[6] give the critical solution temperature for water and o-cresol as 162.8° and for m and p cresols between 140 and 150°). On cooling the autoclave, the phenols separate again from the aqueous layer, as their solubility decreases with decreasing temperature. The drops of phenols, forming in the extract, do not sink to the bottom, but rise to the top, being still hot and specifically lighter than water. In consequence, they redissolve in the layer of oil floating on the top. If this is not taken into account, and the contents of the autoclave are drawn off at the bottom, no indication of separation will be found as might be expected on the

strength of the higher specific gravity of cresols and xylenols at ordinary temperature. This is due to the greater expansion of cresols, which makes them lighter than water at temperatures of 200-300°.

The autoclave was thus modified, so that the aqueous layer could be discharged without cooling, by means of a reducing valve. About two-thirds of the phenolic content of the oil could be extracted at temperatures up to 250°, and the extracts contained 86-98% of phenols. By raising the temperature to 300°, up to 90% of the phenols could be removed, but, at the same time, the solubility of the hydrocarbons increased considerably, so that the extract contained only about 50% of phenols.

The authors conclude that the extraction of phenols with superheated water offers a method of reducing the phenol content of primary tar oils sufficiently for their use as motor fuels, and without the production of waste liquors. The extraction will further remove any products which are soluble in water, even to a slight extent, and there is therefore no question of a corrosive action of refined tar oils on the metal of engines, even in the presence of moisture. It should be noted, that in the two investigations cited, Fischer was working with low temperature tar oils, which contained a considerably higher percentage of tar acids, than is found in coke oven tar oils.

Solutions of Organic Salts as Extraction Media.

No comprehensive investigation of the use of solutions of organic salts to remove tar acids from coal tar distillates has hitherto appeared in the literature. However the following themes in related fields may be considered.

Friedlander in German Patent 181,288 of 1907 uses salts of an aromatic sulfonic acid to render phenols more soluble in water. The solution may be used for disinfectants, etc.

The influence of a third substance on the mutual solubility of phenol and water has been studied by Schreinemakers[7], Timmermans[8], Boutaric and Nabot[9].

Duckett and Patterson[10] investigated the effect of a number of inorganic salts on the Critical Solution Temperature (C. S. T.) of phenol and water, and came to the conclusion, that the effect of

raising the C. S. T. is due to the anions and cations separately, the joint effect being additive. Furthermore, the ions, when arranged in order of their power of elevating the C. S. T. give the Hofmeister series for the coagulation of egg albumin. Thus

$$Na > K > NH_4$$
$$SO_4 > H\ Tartrate > Cl > Br > I = NO_3$$

This paper will be further mentioned in connection with the mechanism of extraction, and steam distillation experiments.

The use of a mixture of tar acids in aqueous sodium oleate as a commercial disinfectant under the trade name of "lysol" calls for mention.

Bailey[11] has studied the ternary system of water-tar acid-sodium oleate, using phenol and each of the three cresols separately.

EXPERIMENTAL.

Carbolic Oil.

Crude carbolic oil was obtained from the Barrett Co. This was the distillate obtained from coke oven tar by the method previously outlined.

The oil was redistilled from a cast iron still and the copious deposit of naphthalene in the distillate was pressed out in an hydraulic press. The residual oil was of a brown yellow color, contained 17.2% by volume of tar acids and had S. G. 25°/25° of 1.026. It gave the following results when 100 cc. was distilled from a 200 cc. flask over a two inch hole in asbestos according to the method laid down by the Barrett Co.

TABLE 1.

F. D.	189°
5%	198
20%	206
60%	230
90%	271
Dry	298

Of the total tar acids present in the oil 33.3% was phenol, C_6H_5OH, as determined by the method of Miller and Urbain,[12] the remainder being a mixture of cresols, with only an insignificant amount of xylenols.

J. B. Hill [13] states that, while the proportions of the three cresols vary considerably with different tars, an average ratio in coke oven tar produced in the United States is about five parts phenol, three parts orthocresol, four parts metacresol, three parts paracresol.

Organic Salts.

To be adaptable to the present scheme of extraction, any organic salt used, must be very soluble in water, must markedly increase the solubility of tar acids in water when present in small quantity, and must be readily obtainable at an attractive price. A number of the commoner aliphatic acid salts were qualitatively examined, without finding one which markedly increased the solubility of phenol in water. An interesting observation was made in the case of succinic acid. Timmermans[8] has noted that free succinic acid greatly lowered the Critical Solution Temperature of phenol and water, which is the same as increasing their mutual solubility at ordinary temperatures. With sodium succinate this effect is much less marked. This accounts for our observation, that, on adding caustic soda to a saturated solution of cresylic acid in aqueous succinic acid, tar acids are precipitated. The action of succinic acid in increasing the solubility of tar acids in water, while of interest in view of the comparative inertness of other aliphatic acids and salts, was not to be compared with the action of the aromatic salts shortly to be considered; so that its action was not further investigated. Sodium oleate and its unusual action, in view of the fact that it is an aliphatic salt, has already been noted.

The magnitude of the effect produced by these organic salts in increasing the solubility of tar acids in water is well brought out by the following table for a typical salt.

Column 1 gives the solubility of the tar acid in water as parts by weight of water required to dissolve 1 part by weight of tar acid at 30°.

Column 2 gives the minimum concentration of sodium paratoluenesulfonate solution which is miscible with its own volume of tar acid at 30°. Concentration is expressed as grams of salt per 100 grams of water. Thus phenol is miscible with its own

volume of a solution of 2.5 g. sodium paratoluenesulfonate in 100 g. water, and orthocresol is miscible with its own volume of a solution of 12.6 g. sodium paratoluenesulfonate in 100 g. water, etc.

TABLE 2.

	Solubility in Water at 30°	Concentration of Aqueous Solution
	1	2
Phenol	10.4	2.5
Orthocresol	33.5	12.6
Metacresol	40	11.5
Paracresol	47	11.55
Cyclohexanol	102	21.8

All of the aromatic salts investigated with the exception of sodium paraphenolsulfonate at once gave positive results. A study was made of the salts of phthalic, benzoic and salicylic acids. The free acids have too low solubilities to be used as such. Timmermans[8] found that free benzoic acid raised the C. S. T. of phenol and water to a small extent whereas salicylic acid had slightly the reverse effect.

The survey of the aromatic salts was then extended to the sulfonic acids, since these are known to form a series of well crystallised, easily soluble salts, and previous work in Columbia laboratories as well as a literature survey had indicated that they showed possibilities in this connection.

The simpler members of the series were first examined, working successively towards those with longer side chain and higher molecular weight.

The sulfonic acid salts used in these experiments were prepared by standard methods and purified by recrystallisation. With the exception of sodium xylenesulfonate and perhaps of sodium cumenesulfonate, they may all be regarded as pure products. The xylene derivative, was prepared by sulfonation of commercial xylene.

According to Beilstein each of the three xylols gives on sulfonating only one product so that the salt prepared would contain the following isomers:

obtained, except with potassium dichromate, the method gave concordant results, and an average precision of one part in two hundred, which was ample for the present research.

It may be noted, that the method gave a precision for cresols which was but slightly less than that for phenol. This difference is due to the greater solubility of bromcresol in water, which in turn gave rise to the phenomenon of the returning blue color of the starch indicator, after the end point has been reached in the titration with sodium thiosulfate. This has caused such a scheme of analysis as applied to cresols, to be discredited by some investigators. It is, however, of minor consequence, if the same duration of water whiteness is taken as end point in each case.

The analytical method used, assumes that the tar acids are extracted in the same proportions in which they are present in the carbolic oil, since the same factor was used for tar acids in residue and tar acids in extract. This factor was determined by standardising the solution against the original carbolic oil. While this assumption is not exactly true, the factors for the individual tar acids differ but slightly, so that the error introduced by using the weighted average factor would be inconsiderable.

The method was further checked during extraction by determining the tar acids in the residual carbolic oil from the last extraction. Tar acids in extracts plus tar acids in residue should equal tar acids originally present. The following case for sodium alphanaphthalenesulfonate is typical.

TABLE 6.

	Tar Acids cc.
1st Extract	2.46
2nd Extract	2.02
3rd Extract	1.62
4th Extract	1.28
Total Tar Acids in Extracts	7.38
Tar Acids in Residue	9.88
Total found	17.26
Total present	17.20

Extraction Experiments.

The extraction of carbolic oil with organic salt solutions was carried out with as close adherence as possible to the methods of larrge scale operation.

As a basis of comparison of the relative efficiencies of the salt solutions used, the tar acids were in each case extracted from 100 cc. of carbolic oil containing 17.2% tar acids by volume. 100 cc. of carbolic oil was shaken successively with the same volume of salt solution in each series of experiments. This treatment was carried as far as ten steps in one case with sodium salicylate, where only 10 cc. of solution was used at each step, but in general, four extractions with 50 cc. solution or four steps with 100 cc. solution was considered to be sufficient.

The carbolic oil and solution were shaken in 250 cc. separatory funnels in a rotating shaker having a speed of 98 r. p. m., for half hour periods. Preliminary investigation showed that equilibrium was reached in about twenty minutes. It was desirable all violent stirring action should be avoided, as this promoted emulsion formation. The type of propeller agitator, commonly used in industry to effect mixing in such cases, should be avoided, since the violent agitation produced in the neighborhood of the propeller would tend to cause emulsions.

Except where otherwise noted, all mixtures showed fairly complete separation in ten minutes, but were allowed to stand considerably longer.

The solutions used were, unless stated to the contrary, saturated with the organic salt at 25° C. The results obtained with saturated solutions did not show such complete extraction, as to permit the use of those of lower concentrations. No experiments were therefore carried out with solutions which were less than saturated at 25° C.

Sodium Salicylate at 25° C.

TABLE 7.

	10 cc. Salt Soln.		25. cc. Salt Soln.		33.3 cc. Salt Soln.	
	Tar Acids cc.	Hydro-carbons cc.	Tar Acids cc.	Hydro-carbons cc.	Tar Acids cc.	Hydro-carbons cc.
1st Extract	1.05	0.2	2.1	0.2	2.4	0.3
2nd "	0.95	0.15	1.8	0.2	2.0	0.2
3rd "	0.95	0.125	1.4	0.2	1.6	0.2
4th "	0.9	0.1	1.1	0.1	1.3	0.15
5th "	0.8	0.1	1.0	0.1	1.1	0.1
6th "	0.8	0.1	0.9	0.1	0.9	0.1
7th "	0.75	0.1				
8th "	0.65	0.1				
9th "	0.6	0.1				
10th "	0.5	0.075				
Total	7.95	1.15	8.3	0.9	9.3	1.05

	50 cc. Salt Solution		100 cc. Salt Solution	
	Tar Acids cc.	Hydro-carbons cc.	Tar Acids cc.	Hydro-carbons cc.
1st Extract	2.75	0.5	4.2	1.0
2nd "	2.2	0.4	3.2	0.9
3rd "	1.8	0.4	2.2	0.8
4th "	1.4	0.4	1.7	0.8
5th "	1.2	0.3	1.3	0.6
6th "	0.9	0.2	1.1	0.5
Total	10.25	2.2	13.7	4.6

Ammonium Phthalate at 25° C.

TABLE 8.

	25 cc. Salt Soln.		50 cc. Salt Soln.		100 cc. Salt Soln.	
	Tar Acids cc.	Hydro-carbons cc.	Tar Acids cc.	Hydro-carbons cc.	Tar Acids cc.	Hydro-carbons cc.
1st Extract	0.67	Nil	1.04	Nil	1.24	Nil
2nd "	0.61	"	0.99	"	1.04	"
3rd "	0.53	"	0.84	"		
4th "	0.48	"	0.78	"		
5th "	0.45	"	0.72	"		
6th "	0.42	"	0.59	"		
Total	3.16		4.96		2.28	

Sodium Phthalate at 25° C.

TABLE 9.

	50 cc. Salt Solution		100 cc. Salt Solution	
	Tar Acids cc.	Hydro-carbons cc.	Tar Acids cc.	Hydro-carbons cc.
1st Extract	0.44	Trace	0.86	Trace
2nd "	0.41	"	0.80	"
Total	0.85		1.66	

Sodium Benzoate at 25° C.

TABLE 10.

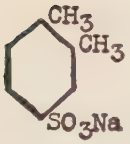
	50 cc. Salt Solution		100 cc. Salt Solution	
	Tar Acids cc.	Hydro-carbons cc.	Tar Acids cc.	Hydro-carbons cc.
1st Extract	2.78	0.3	4.06	0.4
2nd "	1.97	0.2	2.72	0.3
3rd "	1.57	0.1	2.10	0.2
4th "	1.20	0.1	1.78	0.2
Total	7.52	0.7	10.66	1.1

The Aromatic Sulfonic Acid Salts

Sodium Benzenesulfonate at 25° C.

TABLE 11.

	50 cc. Salt Solution		100 cc. Salt Solution	
	Tar Acids cc.	Hydro-carbons cc.	Tar Acids cc.	Hydro-carbons cc.
1st Extract	0.84	Trace	1.54	Trace
2nd "	0.80	"	1.36	"
3rd "	0.77	"	1.12	"
4th "	0.76	"	0.86	"
Total	3.17		4.88	



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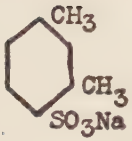

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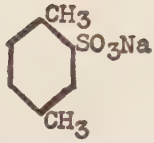

from p-xylene

Their separation, as outlined by Clarke and Taylor[18], is complex and tedious. Since the application of the methods of these workers was not in keeping with the economic purpose of the present investigation, the mixed salts were used as sodium xylenesulfonate without further separation.

Sodium ethylbenzenesulfonate was prepared by the method of Sempotowski [19], who states that the product is exclusively the para salt.

To prepare sodium cumenesulfonate, 100 cc. Eimer and Amend's cumene (purified) was added gradually to a mixture of 80 cc. concentrated sulfuric acid and 20 cc. 50% oleum at room temperature. The product on diluting with water formed two layers, most of the sulfonic acid being contained in the upper layer, which was thus separated from the lower sulfuric acid layer. On treatment with lime and sodium carbonate and evaporating down, a salt, yellow-brown in color similar to recrystallised sodium cymenesulfonate was obtained.

The product is stated [27] to be chiefly para salt with small quantities of the ortho isomer.

Sodium cymenesulfonate was prepared in Columbia Laboratories in Chemical Engineering course s188 by action of 66° sulfuric acid on cymene for four hours. This was recrystallised to give a salt of improved color which consisted almost exclusively of the 1-methyl-4-isopropyl-2-sulfonic acid salt.

After preparing the salts, it was desirable to obtain fundamental data concerning the solubility and density of the saturated solutions, which would be of value in operating the process. Such data is given in Tables 3, 4 and 5. 25° C. was chosen as a convenient operating temperature.

TABLE 3.

Parts of Water required to dissolve 1 Part salt at 25° C.

Ammonium Phthalate	2.38
Sodium Phthalate	4.7
Potassium Phthalate	3.57
Ammonium Benzoate	5.1
Sodium Benzoate	1.62
Potassium Benzoate	12.5
Sodium Salicylate	0.85
Potassium Salicylate	32.3
Sodium Benzenesulfonate	2.24
Sodium o-toluenesulfonate	2.16
Sodium p-toluenesulfonate	1.41
Sodium Xylenesulfonate	0.76
Sodium Ethylbenzenesulfonate	1.12
Sodium Cumenesulfonate	0.87
Sodium Cymenesulfonate	1.01
Sodium α-naphthalenesulfonate	5.80
Sodium β-naphthalenesulfonate	13.2
Sodium Naphthalene 2:7 Disulfonate	2.14
Sodium Benzenemetadisulfonate	2.40

TABLE 4.

Data for Saturated Solution at 25° C.

	S. G.	In 100 cc. Soln.	
	25°/25°	Salt g.	Water g.
Ammonium Phthalate	1.103	32.6	77.7
Sodium Phthalate	1.101	19.3	90.8
Potassium Phthalate	1.135	24.6	88.9
Ammonium Benzoate	1.043	17.1	87.2
Sodium Benzoate	1.150	43.9	71.1
Potassium Benzoate	1.039	7.7	96.2
Sodium Salicylate	1.249	67.6	57.3
Potassium Salicylate	1.024	3.1	99.3
Sodium Benzenesulfonate	1.169	36.0	80.9
Sodium o-toluenesulfonate	1.127	35.7	67.0
Sodium p-toluenesulfonate	1.165	48.4	68.1
Sodium Xylenesulfonate	1.182	67.2	51.0
Sodium Ethylbenzenesulfonate	1.133	53.6	59.7
Sodium Cumenesulfonate	1.165	62.3	54.2
Sodium Cymenesulfonate	1.115	55.5	56.0
Sodium α-Naphthalenesulfonate	1.058	15.6	90.2
Sodium β-Naphthalenesulfonate	1.039	7.3	96.6
Sodium Naphthalene 2:7 Dissulfonate	1.109	35.3	75.6
Sodium Benzenemetadisulfonate	1.177	34.6	83.1

TABLE 5.

Stability in 100 Parts Water at 25° C.

Ammonium Phthalate	42.0
Sodium Phthalate	21.3
Potassium Phthalate	28.0
Ammonium Benzoate	19.6
Sodium Benzoate	61.7
Potassium Benzoate	8.0
Sodium Salicylate	117.8
Potassium Salicylate	3.1
Sodium Benzenesulfonate	44.6
Sodium o-toluenesulfonate	46.4
Sodium p-toluenesulfonate	71.1
Sodium Xylenesulfonate	131.8
Sodium Ethylbenzenesulfonate	89.5
Sodium Cumenesulfonate	115.0
Sodium Cymenesulfonate	98.5
Sodium α-Naphthalenesulfonate	16.73
Sodium β-Naphthalenesulfonate	7.6
Sodium Naphthalene 2:7 Disulfonate	46.9
Sodium Benzenemetadisulfonate	41.6

Analytical Methods.

Tar acids in the extract from carbolic oil by the salt solution were determined as follows. The extract was steam distilled until 100 cc. had passed over, the distillate being collected in a Barrett Type 2 tar acid funnel [15]. Both tar acids and any extracted hydrocarbons passed over into the distillate. 25 cc. of 10% caustic soda solution was then added, and, after shaking, 10 cc. kerosene from a pipette. After further shaking, the two layers were allowed to separate completely, and the increase in volume of the kerosene read off, this giving a direct reading of the tar hydrocarbons extracted by the organic salt solution.

The presence of hydrocarbons in the extract is obviously objectionable, since the purpose of the investigation was to effect as complete a separation as possible, between the tar acids and the non-acidic or hydrocarbon constituents of carbolic oil. The estimation of hydrocarbons could not be carried out with any high de-

gree of accuracy, owing to the presence of only small amounts in a large volume of water. The determination was however sufficiently accurate for the purpose of working out methods for large scale operation.

In experiments with sodium salicylate solution, the tar acids were determined by an extraction method. The tar acids contained in the alkaline layer were liberated by acidfying, taken up in benzene, and the contraction measured on extracting with caustic soda.

In later work, it was found that results could be obtained with greater speed and accuracy by application of the Koppeschaar method as follows:

From 2 to 50 cc. of the sample, depending on tar acid content, is pipetted into a 250 cc. glass stoppered bottle, diluted to 100 cc., five cc. concentrated hydrochloric acid, then five cc. 4% potassium bromide is added, and finally standard potassium bromate is run in from a burette, until a permanent pale yellow color persists. The solution is shaken for five minutes, and allowed to stand fifteen minutes. It is then filtered through a pad of glass wool, packed into the bottom of a filter funnel. After washing, five cc. of 10% potassium iodide is added to the filtrate, and the liberated iodine titrated with standard sodium thiosulfate in the usual manner, until a colorless solution persists for ten seconds.

Due to the conflicting evidence in the literature as to the reliability of this method, it was subjected to searching investigation by standardising the bromate solution against standard solutions of:

1. Potassium dichromate.
2. Carbolic oil analysed by Barrett's extraction and liberation methods[13, 15, 16].
3. Cresylic acid successively refractionated to remove water.
4. Phenol, M.P. 41°.
5. Orthocresol, M.P. 31°.
6. Metacresol, M.P. 10.9°.
7. Paracresol, M.P. 34°.

While a precision of one part per thousand, which has been claimed for the Koppeschaar method by some workers,[17] was not

Sodium Paratoluenesulfonate at 25° C.

TABLE 12.

	50 cc. Salt Solution		100 cc. Salt Solution	
	Tar Acids cc.	Hydrocarbons cc.	Tar Acids cc.	Hydrocarbons cc.
1st Extract	2.32	2.1	4.24	3.1
2nd "	1.72	1.35	2.96	2.0
3rd "	1.40	0.9	1.98	1.5
4th "	1.10	0.75	1.62	1.2
Total	6.54	5.1	10.80	7.8

Sodium Xylenesulfonate at 25° C.

TABLE 13.

	50 cc. Salt Solution		100 cc. Salt Solution	
	Tar Acids cc.	Hydrocarbons cc.	Tar Acids cc.	Hydrocarbons cc.
1st Extract	3.03	8.2	5.62	15.2
2nd "	2.11	6.5	4.20	12.1
3rd "	1.88	5.6	3.54	10.4
4th "	1.60	4.8	3.18	9.4
Total	8.62	25.1	16.54	47.1

Sodium Ethylbenzenesulfonate at 25° C.

TABLE 14.

	50 cc. Salt Solution		100 cc. Salt Solution	
	Tar Acids cc.	Hydrocarbons cc.	Tar Acids cc.	Hydrocarbons cc.
1st Extract	2.90	5.9	5.00	10.5
2nd "	2.21	4.7	3.20	7.2
3rd "	1.53	4.2	2.58	6.2
4th "	1.15	3.8	2.10	5.5
Total	7.79	18.6	12.88	29.4

Sodium Cumenesulfonate at 25° C.

TABLE 15.

	50 cc. Salt Solution		100 cc. Salt Solution	
	Tar Acids cc.	Hydrocarbons cc.	Tar Acids cc.	Hydrocarbons cc.
1st Extract	2.84	7.0	5.06	12.6
2nd "	2.05	5.7	3.38	10.2
3rd "	1.39	5.0	2.38	8.9
4th "	1.20	4.75	2.10	7.8
Total	7.48	22.45	12.92	39.5

Sodium Cymenesulfonate at 25° C.

TABLE 16.

	50 cc. Salt Solution		100 cc. Salt Solution	
	Tar Acids cc.	Hydrocarbons cc.	Tar Acids cc.	Hydrocarbons cc.
1st Extract	2.91	5.3	4.88	10.0
2nd "	2.26	4.4	3.22	7.2
3rd "	1.70	4.0	2.90	6.4
4th "	1.34	3.8	2.58	6.0
Total	8.21	17.5	13.58	29.6

Sodium α-Naphthalenesulfonate at 25° C.

TABLE 17.

	50 cc. Salt Solution		100 cc. Salt Solution	
	Tar Acids cc.	Hydrocarbons cc.	Tar Acids cc.	Hydrocarbons cc.
1st Extract	1.30	0.2	2.46	0.4
2nd "	1.20	0.1	2.02	0.3
3rd "	1.06	Trace	1.62	0.1
4th "	0.94	"	1.28	0.1
Total	4.50		7.38	0.9

Sodium β-Naphthalenesulfonate at 25° C.

TABLE 18.

	100 cc. Salt Solution	
	Tar Acids	Hydrocarbons
	cc.	cc.
1st Extract	1.2	Trace

Sodium Naphthalene 2:7 Disulfonate at 25° C.

TABLE 19.

	50 cc. Salt Solution		100 cc. Salt Solution	
	Tar Acids	Hydrocarbons	Tar Acids	Hydrocarbons
	cc.	cc.	cc.	cc.
1st Extract	0.58	Nil	1.10	Nil
2nd "	0.56	"	1.00	"
3rd "	0.54	"	0.94	"
4th "	0.52	"	0.86	"
Total	2.20		3.90	

Sodium Benzenemetadisulfonate at 25° C.

TABLE 20.

	50 cc. Salt Solution		100 cc. Salt Solution	
	Tar Acids	Hydrocarbons	Tar Acids	Hydrocarbons
	cc.	cc.	cc.	cc.
1st Extract	0.40	Nil	0.82	Nil
2nd "	0.40	"	0.78	"
3rd "	0.38	"	0.76	"
4th "	0.38	"	0.74	"
Total	1.56		3.10	

It was expected that, due to the greatly increased solubility of these organic salts in hot water, extraction at elevated temperatures would be advantageous.

Accordingly, 100 cc. carbolic oil together with 100 cc. of aqueous salt solution was placed in a copper gas sampling tube and heated in an oil bath at 100° C. for an hour. The tube was withdrawn periodically and shaken.

Case 1.

100 cc. carbolic oil extracted with 100 cc. ammonium phthalate solution saturated at boiling, (the salt being soluble in 0.7 parts of water). Extraction at 100° C.

TABLE 21.

	Tar Acids cc.	Hydrocarbons cc.
1st Extract	3.3	Trace
2nd "	2.1	"
Total	5.4	

Case 2.

100 cc. carbolic oil extracted with 100 cc. sodium phthalate solution saturated at boiling (1 part salt soluble in 1.38 parts water). Extraction at 100° C.

TABLE 22.

	Tar Acids cc.	Hydrocarbons cc.
1st Extract	2.84	Trace
2nd "	2.10	"
Total	4.94	

Case 3.

100 cc. carbolic oil extracted with 100 cc. sodium salicylate solution saturated at boiling (1 part salt solution 0.57 parts water). Extraction at 100° C.

TABLE 23.

	Tar Acids cc.	Hydrocarbons cc.
1st Extract	5.2	1.7
2nd "	3.7	1.4
Total	8.9	3.1

Case 4.

100 cc. carbolic oil extracted with 100 cc. sodium benzoate solution saturated at boiling (1 part salt soluble in 1.30 parts water). Extraction at 100° C.

TABLE 24.

	Tar Acids	Hydrocarbons
	cc.	cc.
1st Etxract	4.88	1.0
2nd "	2.84	0.8
Total	7.72	1.8

Case 5.

In order to study the effect of temperature alone, a solution of sodium phthalate saturated at 25° C. (1 part salt soluble in 4.7 parts water) was used as extraction medium at 100° C.

Thus 100 cc. carbolic oil extracted with 100 cc. sodium phthalate solution as above. Extraction at 100° C.

TABLE 25.

	Tar Acids	Hydrocarbons
	cc.	cc.
1st Extract	1.10	Nil
2nd "	0.88	"
Total	1.98	

Case 6.

100 cc. carbolic oil extracted with 100 cc. sodium benzenesulfonate solution, saturated at boiling (1 part salt soluble in 1.03 parts water). Extraction at 100° C.

TABLE 25a.

	Tar Acids	Hydrocarbons
	cc.	cc.
1st Extract	2.82	0.2
2nd "	2.41	0.2
	5.23	0.4

Yields.

The yields of tar acids from carbolic oil range from 1.56 cc. or 9.1% of theory for four extractions with 50 cc. portions of sodium benzenemetadisulfonate, up to 16.54 cc. or 96% of theory with sodium xylenesulfonate (four 100 cc. portions). This compares with a yield of about 95% by the caustic soda processes. As is indicated later, the lower yield is largely offset by the saving of chemicals. For four extractions with 100 cc. solution, the yields from the three salts which appear to be most useful are—

Sodium salicylate	11.3 cc. or 65.5% of theory.
Sodium benzoate	10.60 cc. or 61.9% of theory.
Sodium paratoluenesulfonate	10.80 cc. or 62.8% of theory.

Discussion.

It was concluded that increase in temperature only, without increase in concentration of solution, was of slight advantage.

Use of higher temperatures, together with solutions saturated at boiling, gave improved extraction, the extent of the improvement being dependent upon the ratio of the solubilities at the higher and lower temperatures. For the more soluble salts such as sodium salicylate however the increased yield appeared to be insufficient to offset the increased difficulties of operation.

The case of sodium betanaphthalene sulfonate calls for special notice. After rotating in the shaker for half an hour, emulsions were present, so that the mixture had not separated completely into two layers after standing for a week. The tar acids were thus determined in aliquot parts of the clear solution.

It will be noted, that the saturated solution of this salt has S. G. of 1.039, whereas the S. G. of carbolic oil is 1.026. There is thus insufficient difference in specific gravity between the two liquids to admit of adequate separation, and the use of this salt on a large scale would not be warranted. Further investigation of its properties was therefore discontinued.

It will be seen, that the specific gravity of the saturated solution of the alpha salt is 1.058, which is only slightly higher. The effective difference from carbolic oil, is however nearly three times as great as for the beta salt, and this difference is sufficient

to permit of adequate separation in reasonable time, provided that agitation has not been too violent.

It is well at this stage, to review the results which have been obtained with the fourteen different salts, whose aqueous solutions have been used to extract carbolic oil, to determine whether any general conclusions can be drawn from these results.

The best differential solvents for tar acids are exemplified by those organic salts, in which the benzene nucleus may be brought into aqueous solution, with minimum side chains attached.

Sodium benzoate is thus a better differential solvent than sodium salicylate, so that the greater solubility of the latter salt is to some extent offset by the presence of the OH group in addition to the COOH group.

The solubility of sodium phthalate is so low as to forbid its comparison with the foregoing salts.

Increased solubility of tar acids in any solution, is always accompanied by increased solubility of tar hydrocarbons in the same solution, due to the presence of the tar acids. In choosing a salt to use in this process, it is therefore necessary to balance the difficulty of removing the higher hydrocarbon content against the greater value of the more efficient extraction. Fischer[4, 5] in applying his superheated water process, finds with water only, that increasing solubility of the tar acids, is in all cases attended by increasing solubility of the tar hydrocarbons.

As the size or number of aliphatic side-chains attached to the benzene nucleus in the salt increases, the aqueous solution takes up a greater amount of tar hydrocarbons from carbolic oil. In consequence, as we go from the simpler members to the higher members of a series, such as the sulfonic acid salts, the ratio of tar hydrocarbons to tar acids in the extract rises rapidly. This ratio has risen from about 1 to 50, for sodium benzenesulfonate, to 2 to 1 for sodium cymenesulfonate, with only 17% increase in molar solubility.

This does not hold in the same manner for cases where the side-chains are not predominantly aliphatic.

Sodium benzenemetadisulfonate is thus as good a differential solvent as the monosulfonate.

The alphanaphthalene salts are of greater use than the beta salts but, due to low solubility, the efficiency of neither is high. Both fall far short of the salts of the benzene series. It seems improbable, therefore, that investigation of salts derived from still larger molecules such as anthracene, would yield results of value.

It is interesting to note here, that in opposition to the old adage that "like dissolves like," the sodium naphthalenesulfonates do not show nearly the avidity for tar hydrocarbons (which consist almost entirely of naphthalene and homologues) which is shown by the sodium sulfonates of the benzene homologues.

In nearly all cases, as will be observed, the sodium salt has been used. This has the objection that, as Duckett and Patterson[10] have shown, for equal molal strength of solutions, sodium salts raise the C. S. T. of phenol and water to a greater extent than do potassium of ammonium salts. The sodium salts have the advantage of stability over ammonium salts, and of first cost and, in some cases, of greater solubility also over the potassium salts, so that their use appears to be justified.

Duckett and Patterson have shown, in the same paper, that the property of raising the C. S. T. of phenol and water is the additive properties of the individual ions. If this can be applied, mutatis mutandis, to salts which increase the solubility of phenol in water, the effect of the sodium ion would cancel out, and the differences noted in progressing from one member to another, due allowance being made for difference in solubilities of the salts in water, will be due solely to the organic radicle. This probably holds for such salts in dilute solution, but in cases, such as the present, where the concentrations run as high as 4 gram mols of salt per 1,000 grams of water, the individual effect of the ions must be largely masked by the large amount of unionized salt. The function of such salts in the ternary system salt-water-tar acid will be more fully discussed in a later section.

The amount of tar acids in succeeding extracts was found to fall off exponentially, as is commonly the case in extraction with non-miscible liquids.

Due however to the interfering influence of the hydrocarbons,

results for one series of experiments cannot be calculated from the distribution coefficients obtained from another series of experiments with the same salt, in which different proportions of oil and solution were used.

Removal of Hydrocarbons from the Extract.

The non-acidic portion of carbolic oil, which is designated tar hydrocarbons, or simply hydrocarbons, in this paper, consists chiefly of naphthalene together with naphthalene derivatives, such as methylnaphthalene, the latter being of lower melting point than naphthalene, and serving to keep the mixture liquid at ordinary temperature. There are also present, small amounts of basic bodies, such as pyridine.

This residue from the carbolic oil used, after repeated extraction with caustic soda, had S. G. 25°/25° of 1.012.

On steam distillation, as has been shown, the hydrocarbons pass over, along with the tar acids, into the distillate.

In order to produce an acceptable tar acid for the trade, it is necessary that the major part of the hydrocarbon content of the extract should be eliminated. Complete removal is not obligatory, since the product is to compete with a commercial tar acid containing 10% and upwards of non acidic coal tar oils.

During steam distillation, the tar acids come over as an aqueous emulsion, whose specific gravity lies so close to that of tar hydrocarbons, that prolonged standing is imperative, if adequate separation is to be obtained.

The following alternative methods of separation were therefore examined.

Freezing Experiments.

Preliminary attempts to separate hydrocarbons from tar acids by freezing were abandoned after temperatures down to –77° C. had proved unavailing. While cresylic acid does not solidify at this low temperature, it becomes thick and viscous below –10° C. Small amounts of added naphthalene did not separate, and the viscous nature of the material would have precluded complete separation of the two even if partial solidification had occurred. The study was extended to carbolic oil, to determine its limita-

tions as a means of upgrading this material. It was found that concentration of carbolic oil by freezing could not be carried beyond 25% by volume of tar acids owing to difficulties of separation at the lower temperatures and to the tendency of the liquid portion to thicken without solidifying.

Use of Petroleum Hydrocarbons.

Dry kerosene, which is used extensively as a solvent in analytical determinations of tar acids, was found to be miscible in all proportions with cresylic acid. Addition of a small amount of water, however caused separation into two layers. The distribution of cresylic acid between water and kerosene, water and kerosene plus hydrocarbons, and finally between water and hydrocarbons only, was therefore studied, to find out how far kerosene could be employed to aid in separation of tar hydrocarbons from the aqueous distillate.

In the following experiments, the distribution of 2 cc. cresylic between 50 cc. water and 50 cc. oil, of the composition given, was determined by shaking the mixtures for half hour periods.

TABLE 26.

Composition of Oil Layer.

Kerosene cc.	Tar Hydrocarbons cc.	% of Total Cresylic Acid in Water Layer
50	—	49.4
45	5	37.8
40	10	29.3
35	15	22.7
30	20	17.1
25	25	14.0
—	50	5.9

The addition of 10% of alcohol to the water layer does not alter the distribution to any marked extent; thus,

TABLE 27.

Composition of Oil Layer		Composition of Water-Alcohol Layer		% of Total Cresylic Acid in Water-Alcohol Layer
Kerosene cc.	Tar Hydrocarbons cc.	Water cc.	Alcohol cc.	
50	—	45	5	50.7
25	25	45	5	14.9

The above table is of interest because of the possible use of alcohol to promote the solubility of tar acids in water. Such application would not under the circumstances be justified.

For large amounts of cresylic acid and kerosene or kerosene-tar hydrocarbons in presence of a relatively small amount of water, the following data was obtained on the distribution of the acidic and neutral oil components after shaking for half an hour.

A. 45 cc. Cresylic Acid, 5 cc. Water, 50 cc Kerosene.
B. 45 cc. Cresylic Acid, 5 cc. Water, 45 cc. Kerosene 5 cc. Tar Hydrocarbons.
C. 45 cc. Cresylic Acid, 5 cc. Water, 40 cc. Kerosene 10 cc. Tar Hydrocarbons.
D. 45 cc. Cresylic Acid, 5 cc. Water, 35 cc. Kerosene 15 cc. Tar Hydrocarbons.

TABLE 28.

	In Cresylic Acid Layer		In Neutral Oil Layer	
	Cresylic Acid	Neutral Oil	Cresylic Acid	Neutral Oil
	cc.	cc.	cc.	cc.
A	40.95	11.9	4.05	38.1
B	40.9	19.0	4.1	31.0
C	41.05	25.1	3.95	24.9
D	completely miscible			

Cresylic acid was found to be less soluble in the heavier petroleum hydrocarbons than it was in kerosene. Thus cresylic acid was incompletely miscible with red engine oil when dry, and addition of water merely increased the separation.

The use of the petroleum hydrocarbons in connection with this problem lies however, not so much in their poor solvent properties for tar acids, as in their low specific gravity, so that, mixed with tar hydrocarbons, the separation of the latter from water is accelerated.

Petroleum hydrocarbons may thus be employed in small quantities in the distillate to take up tar hydrocarbons in order that the latter may be separated in a continuous decanter from the aqueous layer.

Filtration of Distillate.

Continuous separation of the acidic distillate from tar hydrocarbons may also be accomplished by filtration. In laboratory operation, excellent separation was obtained by allowing the condensate from steam distillation to drop from the condenser on to an ordinary filter.

All of the hydrocarbons were retained by the filter. With cloth filters of fine texture, almost as complete a separation could be obtained. In a series of experiments, run with sodium benzoate as extraction medium, the tar hydrocarbons on the filter retained a maximum of 5% of the total tar acids, depending on the precise method of operation.

The filter may be combined with continuous decantation of hydrocarbons with good effect. Where petroleum hydrocarbons are added, it is advisable to employ a heavier fraction than kerosene, which displays some tendency to be washed through the filter.

Preparation of Commercial Product.

After removal of hydrocarbons, the tar acids are separated from their aqueous solvent, either by distillation, or, more economically, by extraction with benzene. One extraction with benzene will suffice, if the aqueous residue is used as feed water for a special boiler supplying steam for the steam distillation process, as is common practice in aniline plants. The same water is thus kept in circulation between distillation plant and steam boiler, and loss of material by discharging it to the sewers is avoided.

By fractional distillation, benzene is removed, phenol is separated from cresols, and a dry, commercially acceptable product is readily obtained.

Outline of Process.

At this point it may be well to summarize the process as worked out for extraction at 25° C.

Of the various salts examined, sodium benzoate, sodium salicylate, and sodium paratoluenesulfonate appear to be the most attractive, when items of availibility, cost, and efficiency as an

extraction medium are considered. The use of salts, which give extracts containing relatively large amounts of hydrocarbons, is precluded by the much greater solubility of tar acids in such hydrocarbons, which would result in too great an amount of tar acids being retained by these hydrocarbons in the filtrate.

Carbolic oil, preferably redistilled, is successively extracted with a saturated solution of one of the three salts enumerated above.

Stirring equipment is so designed as to minimize emulsion formation, and is preferably of the rotating shaker type. The extracts are steam distilled, and the extracted hydrocarbons removed from the distillate, either by continuous decantation, after addition of petroleum oils to promote separation, or by filtration through a closely woven cloth filter. The aqueous acidic layer is concentrated by distillation, or extracted with benzene and then fractionated, the benzene being recovered. Aqueous residues are used as boiler feed water to avoid loss. By such a process, use of caustic soda and sulfuric acid or carbon dioxide and lime are entirely avoided, and a product of greater purity may reasonably be expected.

Equilibrium in the System Water-Tar Acid-Sodium Toluene-Sulfonate.

It was of interest to determine the individual solubilities of Phenol and the three cresols in one or two organic salt solutions to find out how widely these individual solubilities varied.

The use of sodium salts of the isomeric toluenesulfonic acids introduced a phase of theoretical interest in studying the relationship if any between the respective solubilities and the orientation of the various side chains attached to the benzene nucleus.

Data on the purity of materials used will be found on page 18 of this study.

The following tables give percentage by weight of each component in equilibrium at 30° C.

System Water-Phenol-Sodium Orthotoluenesulfonate at 30° C.

(See Fig. 1)

TABLE 29.

Water	Phenol	Salt
91.2	8.8	----
89.25	10.0	0.75
86.8	12.0	1.2
83.45	15.0	1.55
78.28	20.0	1.72
68.28	30.0	1.72
58.3	40.0	1.70
48.4	50.0	1.60
38.9	60.0	1.10
34.15	65.0	0.85
32.1	67.5	0.40
30.3	69.7	----

System Water-Orthocresol-Sodium Orthotoluenesulfonate at 30° C.

(See Fig. 2)

TABLE 30

Water	Orthocresol	Salt
97.1	2.9	-----
89.1	2.9	8.0
88.35	3.0	8.65
81.3	10.0	8.7
71.3	20.0	8.7
66.4	25.0	8.6
56.8	35.0	8.2
47.35	45.0	7.65
38.2	55.0	6.8
29.5	65.0	5.5
21.0	75.0	4.0
17.1	80.0	2.9
14.2	84.0	1.8
13.7	86.3	-----

System Water-Metacresol-Sodium Orthotoluenesulfonate at 30° C.

(See Fig. 3)

TABLE 31.

Water	Metacresol	Salt
97.6	2.4	0.0
89.8	2.4	7.8
86.35	5.0	8.65
81.35	10.0	8.65
71.35	20.0	8.65
61.40	30.0	8.60
51.65	40.0	8.35
42.25	50.0	7.75
33.05	60.0	6.95
24.9	70.0	5.1
21.0	75.0	4.0
17.25	80.0	2.75
15.0	83.0	2.0
14.0	84.5	1.5
13.5	86.5	0.0

System Water-Paracresol-Sodium Orthotoluenesulfonate at 30° C.

(See Fig. 4)

TABLE 32.

Water	Paracresol	Salt
97.9	2.1	----
92.9	2.1	5.0
89.9	3.8	6.3
83.4	10.0	6.6
78.2	15.0	6.8
67.95	25.0	7.05
57.2	35.5	7.3
47.8	45.0	7.2
38.5	55.0	6.5
29.8	65.0	5.2
25.5	70.0	4.5
21.8	75.0	3.2
18.3	80.0	1.7
15.6	84.4	----

System Water-Phenol-Sodium Paratoluenesulfonate at 30° C.

(See Fig. 5)

TABLE 33.

Water	Phenol	Salt
91.2	8.8	---
89.25	10.0	0.75
83.8	15.0	1.2
78.64	20.0	1.36
68.6	30.0	1.40
58.63	40.0	1.37
48.78	50.0	1.22
39.08	60.0	0.92
34.6	65.0	0.40
30.3	69.7	---

System Water-Orthocresol-Sodium Paratoluenesulfonate at 30° C.

(See Fig. 6)

TABLE 34.

Water	Orthocresol	Salt
97.1	2.9	---
91.2	4.0	4.8
88.4	6.0	5.6
83.7	10.0	6.3
78.2	15.0	6.8
73.15	20.0	6.85
63.2	30.0	6.8
53.8	40.0	6.2
44.4	50.0	5.6
35.2	60.0	4.8
26.2	70.0	3.8
21.85	75.0	3.15
17.7	80.0	2.3
14.9	84.0	1.1
13.7	86.3	---

ganic salts as are here considered, and when present in the free state, has been observed.

As a result of this, it has been postulated, that molecular combination occurs between such organic salts and water, whereby a new solvent is produced, which may be regarded as occupying a position, and showing properties, intermediate between water and the ordinary organic solvents. If this is the case, then there is present in solution less free water than the analysis would indicate.

In view of the fundamental differences which exist between water and the organic liquids, this bridging of the gap between the two becomes of especial interest.

The theory has been put forward by numerous workers[20, 21, 28] that water consists of a molecular complex, H_4O_2, H_6O_3 or H_8O_4 in equilibrium with H_2O, the latter being the volatile constituent.

It is not our purpose here, to enter this controversy, but to deal only with the variations of water from its normal state, which are the result of hydration of certain organic salts.

If the hypothesis of formation of a new solvent is correct, a tar acid may be expected to show a vapor pressure, when in solution in this solvent, which differs from its vapor pressure in a water solution only. When dissolved in aqueous solutions of salts where no new solvent is present, this vapor pressure will have yet another value. The numerical relation of these values which would be demanded by theory is open to discussion.

One phase of the problem of the "new solvent" hypothesis was attacked by studying the process of steam distillation. Such a study has the dual advantage of testing the hypothesis, and of making an intimate acquaintance with one of the integral steps of our new extraction process.

It may be noted that the use of phenols in this experiment introduces a further possible complication, since phenol has been found [22, 23] to form compounds with many salts, including some of those under discussion. Phenol is considered to play the part of water of crystallization in these cases. Although numerous such compounds have been prepared, they have only been prepared in absence of all trace of water, and are in all cases decom-

posed on addition of water. It would therefore seem unlikely, that molecular combination occurs between phenol and salt in aqueous solution. (See also p. 52.)

Steam Distillation.

The investigation was started using the ordinary set up employed for steam distillation in organic chemistry.

A solution containing 0.0477 G. Mol. cresylic acid (the amount delivered by a 5 cc. pipette) in 50 cc. water or in 50 cc. salt solution was steam distilled, and the rate at which the tar acids passed over was studied.

It quickly became evident that consistent results could not be obtained with such an apparatus, owing to the changing steam supply and to the varying amount of heat transferred from the free flame to the distillation flask. The arrangement was therefore modified as follows. In place of the usual vessel to act as boiler, a small capsule of one and a half inch pipe, two inches long, closed at either end by pipe caps was constructed. The upper cap was drilled and tapped to take an inlet and an outlet tube. An orifice was made out of glass tubing, which delivered ten grams of water per minute under convenient head. The capsule was heated over the free flame and water run into it via the orifice under constant head. The water being vaporised immediately it dropped into the capsule, gave a very satisfactory constant steam supply of ten grams per minute, whose temperature was controlled by reading the thermometer in the outlet pipe. To obtain constant heat transfer, the distillation flask was surrounded by a boiling water bath. Distillation was commenced and a stop watch started when the first drop of distillate fell into the receiver. Fractions were collected in the following time intervals in minutes: 0-1, 1-3, 3-6, 6-10, 10-15, 15-20, 20-25, 25-30, 30-35.

On plotting duplicate experiments, excellent agreement was found. While the rate could not be controlled during the first minute, throughout the remainder of the distillation the curves were almost identical.

The following duplicate runs for 0.0477 G. Mol cresylic acid in 50 cc. water is typical of the agreement obtained.

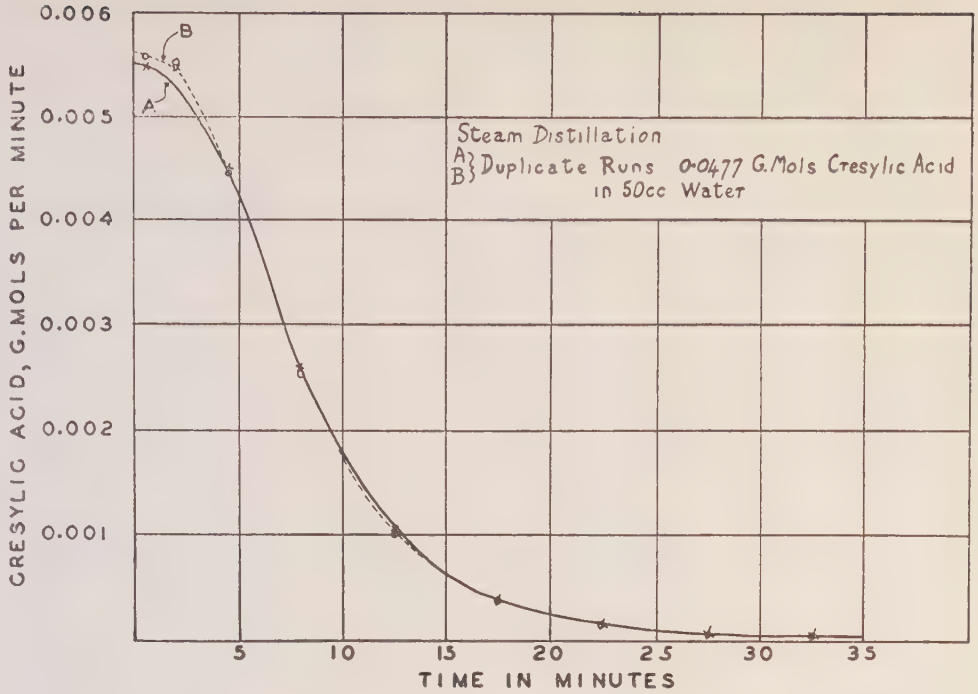
0.006
0.005
0.004
0.003
0.002
0.001
CRESYLIC ACID, G.MOLS PER MINUTE
5
10
15
20
25
30
35
TIME IN MINUTES
B
A
Steam Distillation
A } Duplicate Runs 0.0477 G.Mols Cresylic Acid
B } in 50cc Water

FIG 9

TABLE 37.

Time Interval Minutes	Average Time Minutes	G. Mols. Cresylic Acid per Minute Expt. 1. A	Expt. 2. B	Average C
0-1	0.5	0.00546	0.00556	0.00551
1-3	2.0	0.00546	0.00551	0.00549
3-6	4.5	0.00452	0.00447	0.00450
6-10	8.0	0.00259	0.00252	0.00256
10-15	12.5	0.00103	0.00098	0.00101
15-20	17.5	0.00037	0.00037	0.00037
20-25	22.5	0.00013	0.00013	0.00013
25-30	27.5	0.000057	0.000052	0.000055
30-35	32.5	0.000028	0.000021	0.000025

The data of Experiments 1 and 2 above are plotted in Fig. 9, the two curves being labelled A and B respectively. It will be noted that the two curves are not sufficiently far apart to be clearly distinguishable.

For 0.0477 G. Mol. cresylic acid in 50 cc. sodium alpha-naphthalenesulfonate (saturated solution at 25°) the results were:

TABLE 38.

Average Time Minutes	G. Mols. Cresylic Acid per Minute. D.
0.5	0.00470
2.0	0.00440
4.5	0.00366
8.0	0.00267
12.5	0.00158
17.5	0.00083
22.5	0.00040
27.5	0.00022
32.5	0.00012

The data of this table, in which D is the average of two runs, is plotted in Fig. 10, where C is the curve for cresylic acid in water from Table 37, and D is the plot for cresylic acid in sodium alphanaphthalenesulfonate.

Curves A, B and C of Figs. 9 and 10 are the only cases where considerable change in curvature occurs in the first two minutes of distillation. As has been stated, this portion of these curves

System Water-Metacresol-Sodium Paratoluenesulfonate at 30° C.

(See Fig. 7)

TABLE 35.

Water	Metacresol	Salt
97.6	2.4	----
91.25	3.0	5.75
88.95	5.0	6.05
83.8	10.0	6.2
73.8	20.0	6.2
63.8	30.0	6.2
53.8	40.0	6.2
43.9	50.0	6.1
34.5	60.0	5.5
25.8	70.0	4.2
21.6	75.0	3.4
17.9	80.0	2.1
15.15	84.0	0.85
13.5	86.5	----

System Water-Paracresol-Sodium Paratoluenesulfonate at 30° C.

(See Fig. 8)

TABLE 36.

Water	Paracresol	Salt
97.9	2.1	----
93.0	3.0	4.0
90.15	5.0	4.85
84.8	10.0	5.2
74.35	20.0	5.65
64.3	30.0	5.7
54.25	40.0	5.75
44.5	50.0	5.5
35.2	60.0	4.8
22.35	75.0	2.65
18.65	80.0	1.35
15.6	84.4	----

The above data has been plotted in Fig. 1-8. The deleted apex of the triangle represents 100% organic salt in each case. It will be noted at once how much more easily phenol is taken up by a dilute solution of sodium toluenesulfonate than are the cresols.

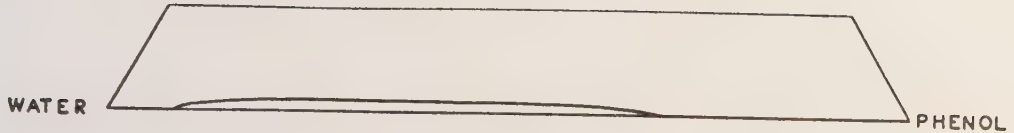

FIG 1

FIG 2

FIG 3

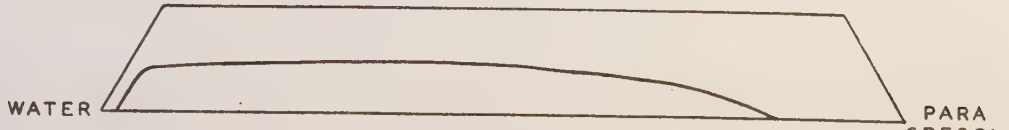

FIG 4

SYSTEM WATER TAR ACID SODIUM ORTHOTOLUENESULFONATE AT 30°

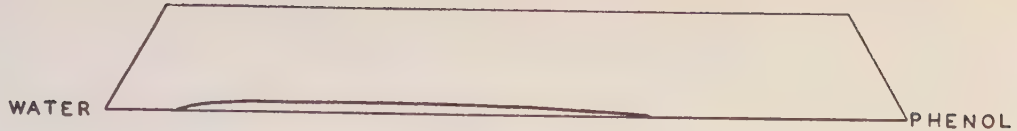

FIG 5

FIG 6

FIG 7

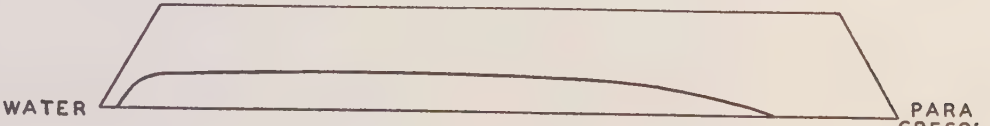

FIG 8

SYSTEM WATER TAR ACID SODIUM PARATOLUENESULFONATE AT 30°

Phenol is miscible in all proportions with 1.72% of the ortho salt in the mixture or with an aqueous solution of about 3% strength.

With the para salt a slightly weaker solution will suffice.

It also becomes evident that the solubility of phenol and each of the three cresols in water is increased to a greater extent by the para salt than by the ortho salt, more of the latter being required to produce complete miscibility.

This is advantageous since firstly the para salt is a cheaper material, being produced as a by product though in greater quantity than the ortho salt when the latter is prepared as an intermediate in the saccharin industry; secondly, in view of the fact that the para salt is more soluble, a saturated solution of the para salt will be doubly the more efficient as an extraction medium.

Considering the cresols individually, the ortho salt promotes solution of paracresol most easily (Fig. 4) and has less effect on the other two cresols which give almost identical curves (Figs. 2 and 3).

The para salt gives similar results, promoting solution of the paracresol most easily (Fig. 8) and has much the same effect on the ortho and meta cresol whose curves indicate similar solubility but differ somewhat in shape.

It is of interest to compare the above with the results of Bailey[11] who investigated the solubility of phenol and each of the three cresols in aqueous sodium oleate solution at 20° C.

The sodium toluene sulfonates are better solvents for tar acids in aqueous solution than is sodium oleate.

The greater solubility of phenol is also noted by Bailey but the ortho cresol is in his case, the most soluble cresol.

The binodal curves obtained by Bailey are similar in shape to Figs. 1-8 though the maximum in the curve occurs near to the cresol rather than the water boundary.

STUDY OF THE MECHANISM OF SOLUTION OF TAR ACIDS.

In the course of numerous experiments in cognate fields, carried out in Columbia laboratories, a marked difference in properties between the solvent (water), when associated with such or-

is the least reliable, and it is uncertain whether this change of curvature is a characteristic of cresylic acid water mixtures, or whether it is due to the tar acids initially evolved clinging to the walls of the Liebig condenser and being carried over later.

It will be noted in the case of Figs. 10, 11 and 13, that, whereas the distillation of tar acids is at first more rapid for one solution than for the other, a reversal takes place and the tar acids finally distil more slowly from the first solution. This is of course due to the exhaustion of the supply of tar acids, since the concentration in the two solutions is equal only when t is O. The curves may be checked by determining the area under them. Since G. Mols per Minute by minutes gives G. Mols this area will give the total tar acids distilled over up to $t = 35$.

Thus for plot E the area determined by calculation from the original data gives 0.0477 G. Mols and by cutting out and weighing 0.0475 G. Mols; plot F gives 0.0484 G. Mols by both methods. These results are apparently slightly high when it is remembered that there must be some residual cresylic acid at $t = 35$.

The research was then extended to phenol and the following data obtained:

E. for 0.0477 G. Mol phenol in 50 cc. water.
F. for 0.0477 G. Mol phenol in 50 cc. sodium alphanaphthalenesulfonate (saturated solution at 25°)

TABLE 39.

Average Time	G. Mols. Phenol per Minute.	
Minutes	E.	F.
0.5	0.00601	0.00345
2.0	0.00550	0.00326
4.5	0.00403	0.00292
8.0	0.00208	0.00236
12.5	0.00111	0.00178
17.5	0.00050	0.00109
22.5	0.00020	0.00066
27.5	0.00009	0.00033
32.5	0.00004	0.00019

These results are plotted in Fig. 11. It will be seen that the volatilisation of phenol during steam distillation is even more modified than in the case of cresylic acid by the presence of an

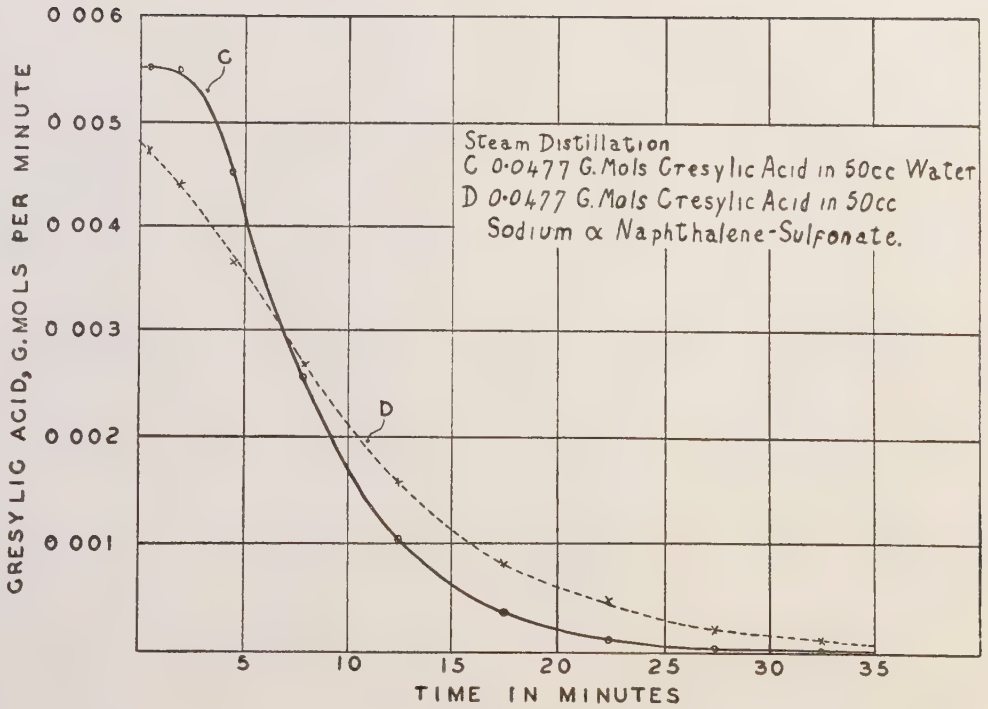
0 006
0 005
0 004
0 003
0 002
0 001
CRESYLIC ACID, G. MOLS PER MINUTE
C
D
Steam Distillation
C 0·0477 G. Mols Cresylic Acid in 50cc Water
D 0·0477 G. Mols Cresylic Acid in 50cc
Sodium α Naphthalene-Sulfonate.
5
10
15
20
25
30
35
TIME IN MINUTES

FIG 10

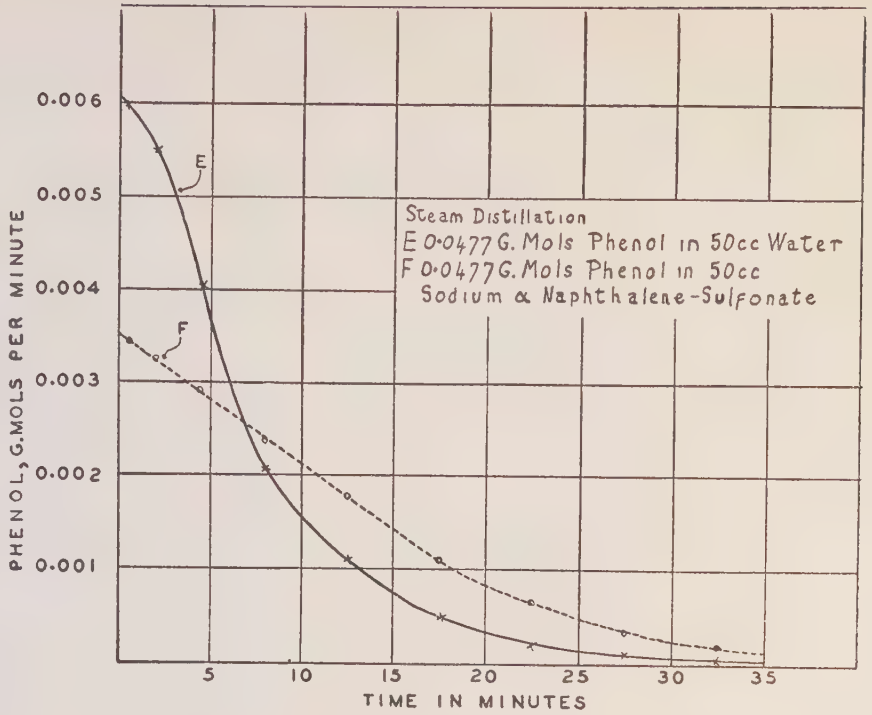
Steam Distillation
E 0·0477 G. Mols Phenol in 50cc Water
F 0·0477 G. Mols Phenol in 50cc
Sodium α Naphthalene-Sulfonate
E
F
PHENOL, G.MOLS PER MINUTE
0.006
0.005
0.004
0.003
0.002
0.001
5
10
15
20
25
30
35
TIME IN MINUTES

FIG 11

organic salt. It will be noted that the major part of plot F shows a linear relation between rate and time.

To determine whether this linear relation was peculiar to phenol solutions of this concentration, further distillations were carried out, using one-half the amount of phenol and double the amount in the same volume of salt solution.

G. 0.02385 G. Mol. phenol in 50 cc. sodium alphanaphthalenesulfonate (saturated solution at 25°)

H. 0.0954 G. Mol. phenol in 50 cc. sodium alphanaphthalenesulfonate (saturated solution at 25°)

TABLE 40.

Average Time Minutes	G. Mols. Phenol per Minute. G.	H.
0.5	0.00199	0.00601
2.0	0.00178	0.00533
4.5	0.00151	0.00500
8.0	0.00112	0.00460
12.5	0.00084	0.00338
17.5	0.00039	0.00195
22.5	0.00022	0.00112
27.5	0.00012	0.00059
32.5	0.00007	0.00033

Fig. 12, which represents the above data, together with D of Table 38, repeated for comparison, shows the linear relation to be fortuitous.

After having made several runs with a salt such as sodium alphanaphthalenesulfonate, which greatly increased the solubility of phenol in water, it was of interest to study the distillation curve of a salt which decreases the solubility of phenol in water. Sodium chloride was selected as a typical salt of this type, since its action in this respect has been the subject of extensive study[8].

The sodium chloride solution was of the same molality, i. e., the same number of mols per 1,000 g. water as the sodium alphanaphthalenesulfonate, namely 42.5 g. in 1,000 g. water.

Thus for 0.0477 G. Mols phenol in 50 cc. of this sodium chloride solution, the distillation rates were:

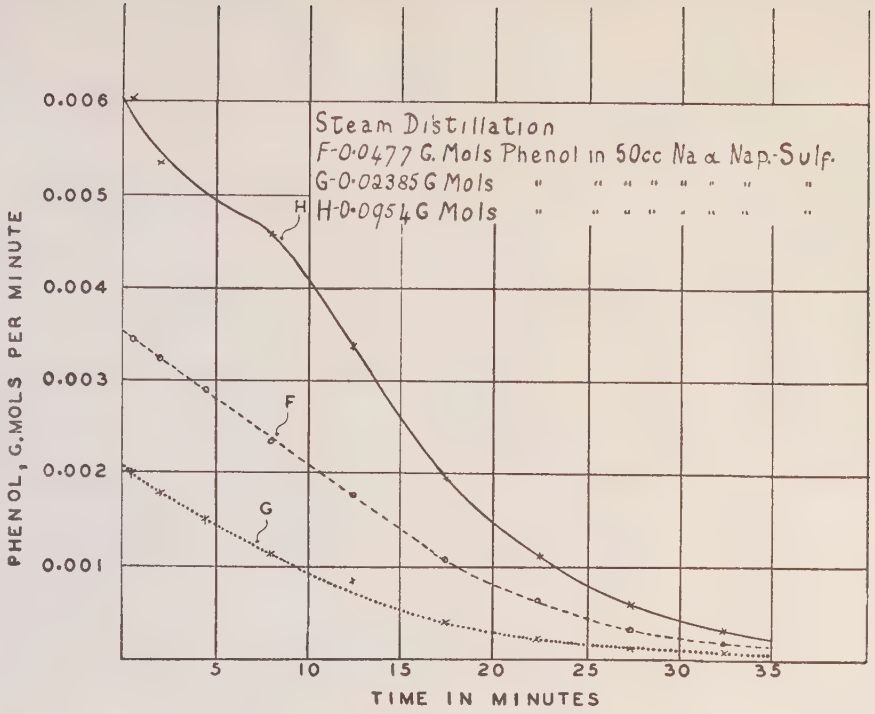
Steam Distillation
F-0·0477 G. Mols Phenol in 50cc Na α Nap-Sulf.
G-0·02385 G Mols " " " " " " "
H-0·0954 G Mols " " " " " " "
H
F
G
0.006
0.005
0.004
0.003
0.002
0.001
PHENOL, G.MOLS PER MINUTE
5
10
15
20
25
30
35
TIME IN MINUTES

FIG 12

TABLE 41.

Average Time Minutes	G. Mols. Phenol per Minute. J.
0.5	0.0073
2.0	0.0060
4.5	0.0042
8.0	0.00166
12.5	0.00074
17.5	0.00030
22.5	0.000104
27.5	0.000048
32.5	0.000021

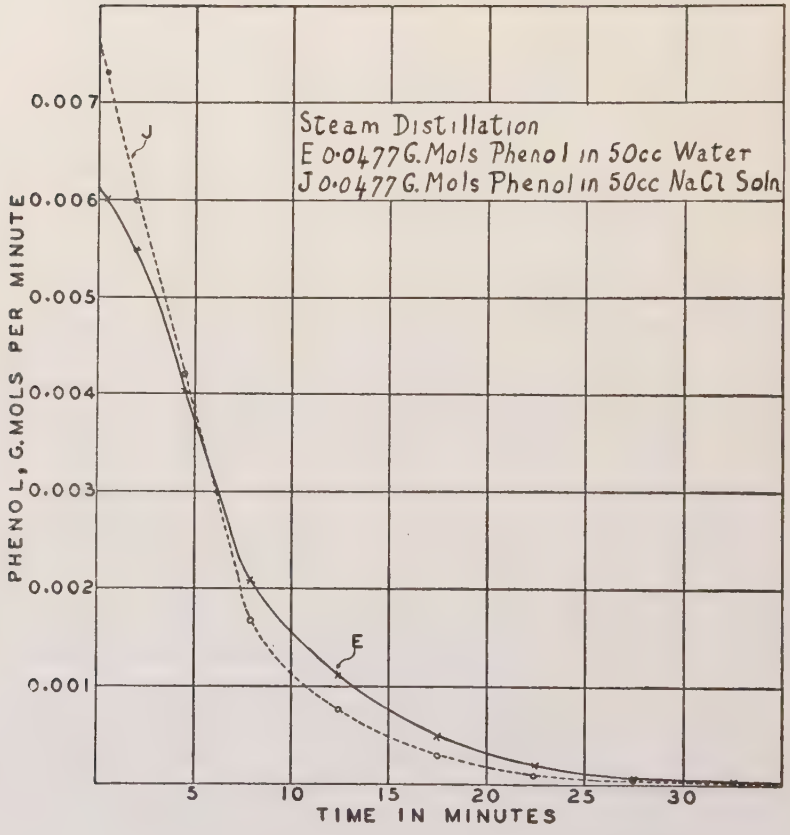

FIG 13

As will be seen from Fig. 13, in which this data, together with C of Table 37, (phenol in water) has been plotted, the presence of sodium chloride accelerates the rate of steam distillation, though, due to the sharp slope of both curves, the effect is not as marked as it would otherwise be. A possible explanation of this accelerated rate is that sodium chloride forms a hydrate in which phenol is insoluble, though soluble in the free water accompanying it. If the organic salt forms a hydrate in which phenol is more readily soluble than in the free water accompanying it, then the three distillation curves of Figs. 11 and 13 would be just what would be predicted by our hypothesis.

Furthermore, as is shown in Fig. 14 where the logarithm of

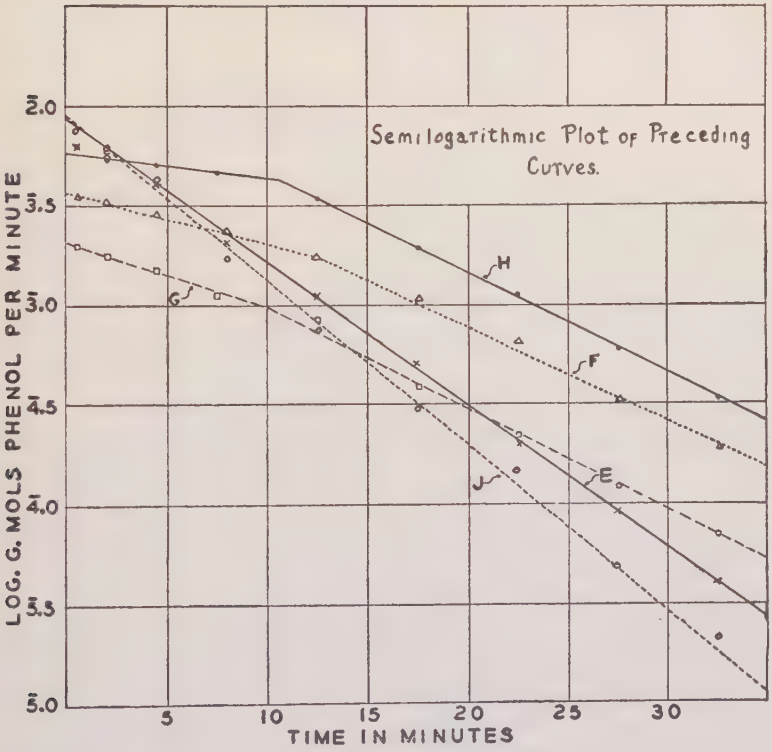

FIG 14

columns E. F. G. H and J of Tables 39-41 is plotted against time in minutes, we find that these plots agree with the equation

$$\frac{dx}{dt} = \text{Log Concn.} + \text{Const.}$$

Where x = G. Mols. Tar Acid per Minute. t = time in minutes.

For phenol water mixtures, two straight lines are necessary to fit the data of the semilogarithmic plot.

We regard this straight line relation as excellent evidence of the absence of compound formation between phenol and water or phenol and salt at the distillation temperature.

The observation of Duckett and Patterson[10], that the ions, when arranged in order of elevating the "critical solution temperature" (C. S. T.) of phenol water mixtures, give the Hofmeister series for the coagulation of egg albumin, is of interest. It is probable that if the series of salts used by Duckett and Patterson, were applied to the present investigation, using solutions of the same molality as used for sodium chloride, a series of curves would be obtained, whose slopes, arranged in order of magnitude, would give a series similar to the Hofmeister series, $Cl > Br > I = NO_3$. Taylor and Pollard [24] found that the series $Cl < Br < I < NO_3$ holds good almost without exception as the order of increasing degree of association of similarly constituted salts in solution. The inverse relation between these two series does not appear to have been previously noted. The obvious inference is that the power of raising the C. S. T. is a function of the degree of association of the salt. Such a conclusion is confronted with the absence of evidence to show that inorganic salts, such as the sodium halides, are associated in aqueous solution, and also with the somewhat illusory nature of the Hofmeister series. It would further lead to the absurdity that the present salts are dissociated.

Loeb has shown[25], that Hofmeister and other earlier workers did not take into consideration the varying effect of the salts in which these ions were present, on the hydrogen ion concentration of the solution. He has shown, that, if care is taken to adjust the pH to a common value before comparison is made, the numerous complex Hofmeister series may be replaced by a simple valency rule. The Hofmeister series are therefore meaningless.

In connection with the new solvents, the question of pH is of minor importance, for, within fair limits, the solubility of phenolic bodies is independent of the pH of the salt solutions.

It may be noted moreover, that according to Turner and English [26] formation of compounds does not depend on prior association of the constituents. The same authors conclude that the influence of the solvent does not appear to be the same in the two cases, and that forces producing molecular combination appear to be different in origin or act differently from those causing molecular association, the latter being considered by them to be of electrical origin.

We may conclude, therefore, that a survey of the literature presents nothing contrary to the hypothesis of the formation of a new organic solvent by the hydration of organic salts in nearly saturated solutions, whereas our own experiments afford strong evidence to support it.

SUMMARY.

1. It has been noted, that the only commercially successful method of removing tar acids from coal tar, is the staple one, which requires the use of alkali and acid.
2. Other processes described in the literature have been reviewed.
3. The need for a cheaper method of extracting tar acids from coal tar, to enable this tar to continue as a source of tar acids in competition with new developments, has been emphasized.
4. A new method of extracting tar acids from coal tar oils has been described which is believed to satisfy this need.
5. Fundamental data of value in operating such a process has been presented.
6. The process avoids the consumption of chemicals, but requires more extensive distillation than the older one.
7. The process consists of the following steps:
   (a) Extraction of tar acids from coal tar oils by a concentrated aqueous solution of an aromatic organic salt.
   (b) Steam distillation of the extract, whereby tar acids and extracted hydrocarbons are expelled.
   (c) Removal of hydrocarbons from the distillate.

(d) Concentration of the tar acids in the distillate to yield an acceptable commercial product.

8. The ternary system water, tar acid, sodium toluenesulfonate, has been studied and binodal curves for eight such systems have been drawn.
9. The mechanism of steam distillation, as applied to this process, has been the subject of extended study, and important evidence regarding the mode of extraction of tar acids by organic salt solutions has been obtained.

LITERATURE CITED

[1] Chem. Met. Eng., **37,** 33, (1930).
[2] E. Baumann, Ber., **10,** 686 (1877).
[3] Fischer, Tropsch and Breuer, Brennstoff Chem. **3,** 1, (1922).
[4] F. Fischer, Brennstoff Chem., **4,** 225, 241, (1923).
[5] Fischer and Lessing. The Conversion of Coal into Oils. Van Nostrand.
[6] Sidgwick, Spurrell and Davies, J. Chem. Soc., **107,** 1202, (1915).
[7] Schreinemakers, Z. Physikal Chem., **29,** 577 (1899), **33,** 78 (1900).
[8] Timmermans, Z. Physikal Chem., **58,** 129-213 (1907).
[9] Bontaric and Nabot, Compt. Rend., **176,** 1618 (1923).
[10] Duckett and Patterson, J. Phys. Chem., **29,** 294, (1925).
[11] C. R. Bailey, J. Chem. Soc., **123,** 2559, (1923).
[12] Miller and Urbain, J. Ind. Eng. Chem. Analyt. Ed., **2,** 123, (1930).
[13] J. B. Hill, Allen's Commercial Organic Analysis, 5th Ed., Blakiston (Vol. 3).
[14] Hamilton, Hickson and Patterson, J. Chem. Soc., **127,** 2544 (1925).
[15] J. M. Weiss, J. Ind. Eng. Chem., **10,** 914, (1918).
[16] J. B. Hill, J. Ind. Eng. Chem., **15,** 799 (1923).
[17] Redman, Weith and Brock, J. Ind. Eng. Chem., **5,** 389, 831, (1913).
[18] Clark and Taylor, J. Am. Chem. Soc., **45,** 830 (1923).
[19] Sempotowski, Ber., **22,** 2663 (1889).
[20] W. E. S. Turner, Molecular Association. Longmans Green 1915.
[21] J. Kendall, J. Am. Chem. Soc., **42,** 2478 (1920).
[22] H. Byk, German Patent 100,418 (1898).
[23] Gentsch, German Patent 156,761, 157,616 (1904).
[24] Taylor and Pollard, J. Chem. Soc., **105,** 1751 (1914).
[25] Pryde, Recent Advances in Biochemistry. Blakiston, 1926.
[26] Turner and English, J. Chem. Soc., **105,** 1786 (1914).
[27] Beilstem, Handbuch das Organischen Chemie.
[28] Guye et al, Trans. Far. Soc., **6,** 71-123 (1910).

VITA.

Theodore Cynric Lloyd was born in Natal, South Africa on March 24, 1901. He received his early education in that country and graduated with B.S. in Chemistry from the University of South Africa in 1921. He spent the next two years in graduate study and research in chemical engineering, with special reference to fuels and combustion, at the Imperial College, London, where he worked in the private laboratory of Prof. W. A. Bone, and graduated M.S. (Lond), D.I.C. in 1923.

During the period 1923-28 he was employed as operator, combustion engineer, and research engineer in Coke Oven and Open Hearth divisions of steel mills in Pittsburgh and Cleveland districts. He investigated various problems in the sphere of coal and has published one of these in Chem. Met. Eng., 37, 169 (1930) under the title "New Criterion for Coking Value of Coal."

In September 1928 he entered the Department of Chemical Engineering of Columbia University to carry on graduate work.

Since September, 1929, he has been Instructor in Chemical Engineering at Yale University.

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